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(54) Title: TREATING SLURRIES

(57) Abstract: This invention relates to a composition for treating inorganic slurries and to a method of treating inorganic slurries with the aforesaid composition so as to maintain the slurries in a substantially homogeneous phase. The composition comprises a THP⁺ salt and a dispersant selected from the group consisting of: (i) phosphonated compound containing at least one tertiary nitrogen atom; (ii) phosphonated oligomers of unsaturated acids; (iii) homopolymers of unsaturated acids; and (iv) Polyphosphates The THP⁺ salt is preferably THPS

TREATING SLURRIES

This invention relates to a composition for treating inorganic slurries and to a method of treating inorganic slurries with the aforesaid composition
5 so as to maintain the slurries in a substantially homogeneous phase.

The present invention will be described herein with particular reference to calcium carbonate-based slurries, especially those used in paper-making processes, although it is not to be construed as being limited thereto.

10

Most inorganic slurries contain about 70% to 80% by weight of solids. Many inorganic slurries (particularly those based on calcium carbonate) are known to be susceptible to bacterial contamination and it has been the practice to add one or more biocidally-active materials to the slurries in
15 order to minimise such contamination.

20 Phosphorus-containing compounds, in particular tetrakis(hydroxyorgano)phosphonium salts (THP⁺ salts) are known to be effective biocides. Experimental work carried out by the applicants has shown, for example, that the addition of a solution of tetrakis(hydroxymethyl)phosphonium sulphate (THPS) to a calcium carbonate-based slurry can give rise to a reduction in bacterial count of 10⁴ in 2 hours.

25 However, it is also known that addition of THPS alone to a slurry results in instantaneous heterogeneous thickening and aggregation of the slurry.

30 The applicants have found that the use of a composition comprising a THP⁺ salt and a dispersant will provide continuing preservation against bacterial contamination, while at the same time maintaining the slurry in a substantially homogeneous phase.

Accordingly, in a first aspect, the present invention provides a composition for treating an inorganic slurry, the composition comprising:

5 (a) a tetrakis(hydroxyorgano)phosphonium salt (hereinafter THP⁺ salt);

and

(b) a dispersant selected from the group consisting of:

10

(i) phosphonated compounds containing at least one tertiary nitrogen atom;

(ii) phosphonated oligomers of unsaturated acids;

15

(iii) homopolymers of unsaturated acids;

and (iv) polyphosphates.

20 In accordance with the present invention, the THP⁺ salt is preferably tetrakis(hydroxymethyl)phosphonium sulphate.

Alternatively, the THP⁺ salt may be tetrakis(hydroxymethyl)phosphonium chloride, phosphate, nitrate or oxalate.

25

A preferred example of a dispersant of the type (b)(i) is a compound having one tertiary nitrogen atom, such as a sodium salt of nitrilo-tris(methylene phosphate), particularly the tetra-sodium salt.

30 Preferred examples of dispersants of the type (b)(ii) include those oligomers having the general $H(CH_2OM.CH_2OM)_nPO_3M_2$, wherein M is a

cationic species such that the oligomer is soluble in water and n is a number greater than 1.

Other suitable oligomers are disclosed in the applicant's European Patent
5 Specification 0 491 391.

A preferred example of a dispersant of the type (b)(iii) is a homopolymer of acrylic acid, especially a homopolymer having a molecular weight in the range 2000 to 5000.

10

Preferred examples of dispersants of the type b(iv) include sodium tripolyphosphate.

15

In a second aspect, the present invention provides a method of treating an inorganic slurry to maintain the slurry in a substantially homogeneous phase, the method comprising the addition to the slurry of an effective amount of a composition according to the first aspect of the present invention.

20

The inorganic slurry may, for example, comprise a calcium carbonate-based slurry.

Alternatively, the inorganic slurry may comprise a pigment slurry, a clay slurry or a cement slurry.

25

Preferably, the ratio of THP⁺ salt to dispersant in the composition is about 2:1 (as active ingredients).

30

Suitably, the composition may be added to the slurry in an amount in the range 10ppm to 1000ppm (by weight of the slurry), for example about 750ppm (by weight of the slurry).

The present invention will be illustrated by way of the following examples.

5 In the examples, a 75% calcium carbonate slurry (commercially known as Setacarb) was treated with:

Example 1 : THP⁺ salt alone.

10 Example 2 : THP⁺ salt and dispersant of type (b)(i).

Example 3 : THP⁺ salt and dispersant of type (b)(ii).

15 The amounts of each additive used, and the results, are given in the TABLE below.

TABLE

	Example No.	THP ⁺ salt (ppm)	Dispersant (ppm)	Result
20	1	(a) THPS 750ppm	(b) (nil)	Instant heterogeneous thickening
25	2	(a) THPS 750ppm	b(i) 375ppm	No thickening
30	3	(a) THPS 750ppm	b(ii) 375ppm	No thickening

Notes to TABLE

(a) An aqueous solution of tetrakis(hydroxymethyl)phosphonium sulphate (75% a.i.), available as TOLCIDE®-PS75.

5

(b)(i) An aqueous solution of the tetra sodium salt of nitrilo-tris(methylene phosphonic acid), available as BRIQUEST® 301-32S.

10 (b)(ii) A homopolymer of polyacrylic acid, having a molecular weight in the range 2000-5000 and available as BEVALOID®211.

CLAIMS

1. A composition for treating an inorganic slurry, the composition comprising:

5

(a) a tetrakis(hydroxyorgano)phosphonium salt (herein THP⁺ salt);

and

10 (b) a dispersant selected from the group consisting of:

(i) phosphonated compounds containing at least one tertiary nitrogen atom;

15 (ii) phosphonated oligomers of unsaturated acids;

(iii) homopolymers of unsaturated acids;

and (iv) polyphosphates.

20

2. A composition according to Claim 1, in which the THP⁺ salt is tetrakis(hydroxymethyl)phosphonium sulphate.

25 3. A composition according to Claim 1, in which the THP⁺ salt is tetrakis(hydroxymethyl)phosphonium chloride, phosphate, nitrate or oxalate.

30 4. A composition according to any one of Claims 1 to 3, in which the dispersant (b(i)) is a phosphonated compound containing one tertiary nitrogen atom.

5. A composition according to Claim 4, in which the dispersant (b(i)) is a sodium salt of nitrilo-tris(methylene phosphonate).
6. A composition according to Claim 5, in which the salt is the tetra-
5 sodium salt.
7. A composition according to any one of Claims 1 to 3, in which the dispersant (b(ii)) is a phosphonated oligomer of maleic acid.
- 10 8. A composition according to Claim 7, in which the oligomer has the general formula $H(CH_2OM.CH_2OM)_n PO_3M_2$, wherein M is a cationic species such that the oligomer is soluble in water and n is a number greater than 1.
- 15 9. A composition according to any one of Claims 1 to 3, in which the dispersant (b(iii)) is a homopolymer of acrylic acid.
10. A composition according to Claim 9, in which the homopolymer has a molecular weight in the range 2000 to 5000.
- 20 11. A composition according to any one of Claims 1 to 3, in which the dispersant (b(iv)) is sodium tripolyphosphate.
12. A method of treating an inorganic slurry to maintain the slurry in a substantially homogeneous phase, the method comprising the addition to the slurry of an effective amount of a composition according to any one of Claims 1 to 11.
- 30 13. A method according to Claim 12, in which the ratio of THP⁺ salt to dispersant in the composition is about 2:1 (as active ingredients).

14. A method according to Claim 12 or 13, in which the composition is added to the slurry in an amount in the range 10ppm to 1000ppm (by weight of the slurry).

5 15. A method according to Claim 14, in which the composition is added to the slurry in an amount of about 750ppm (by weight of the slurry).

16. A method according to any one of Claims 12 to 15, in which the
10 slurry comprises a calcium carbonate-based slurry.

17. A method according to any one of Claims 12 to 15, in which the slurry comprises a pigment slurry, a clay slurry or a cement slurry.

15 18. A method of treating an inorganic slurry, substantially as hereinbefore described with reference to the Examples.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N57/34 D21H21/36 D21H19/46 D21H19/58 D21H19/64
 C09C1/02 C04B14/28
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N D21H C09C C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/08127 A (FIDOE STEPHEN DAVID ; JONES CHRISTOPHER RAYMOND (GB); RHODIA CONS SPEC) 31 January 2002 (2002-01-31) page 3, line 25 - page 4, line 4 page 4, line 25 - page 5, line 9 page 8, line 5 - line 10 page 14, line 19 - page 15, line 2; claims 1,9,14,29,39,46 ----- US 6 180 056 B1 (COMSTOCK DANIEL L ET AL) 30 January 2001 (2001-01-30) column 1, line 55 - column 2, line 6 column 3, line 63 - column 5, line 22; claims 1,4,23,24 ----- -/-	1-11
X		1-6,9,10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- *A* document defining the general state of the art which is not considered to be of particular relevance
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/GB2004/000056

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99/33345 A (JONES CHRISTOPHER RAYMOND ; ALBRIGHT & WILSON UK LTD (GB); TALBOT ROBE) 8 July 1999 (1999-07-08) page 1, paragraph 3 – paragraph 4 page 4, last paragraph page 5, paragraph 3 page 6, line 8 – line 17 page 7, last paragraph – page 9, paragraph 2 page 16, last paragraph – page 17, paragraph 2; claims 1,2,12 -----	1-3,7-10
Y	WO 00/04777 A (ECC INT INC) 3 February 2000 (2000-02-03) page 1, line 10 – line 14 page 2, line 21 – page 3, line 5 -----	1-18
A	US 4 673 509 A (DAVIS KEITH P ET AL) 16 June 1987 (1987-06-16) column 1, line 4 – line 38 column 2, line 48 – line 55 column 3, line 1 – line 17 column 3, line 55 – column 4, line 5; example 8 column 11, line 1 – line 13; claims 1,14 -----	1-18
A	EP 0 839 956 A (ECC INT LTD) 6 May 1998 (1998-05-06) column 1, line 9 – column 2, line 56 column 3, line 18 – line 27 column 4, line 5 – line 19; claims; example 1 -----	1-18
A	US 3 597 251 A (KAUFMAN DANIEL) 3 August 1971 (1971-08-03) column 2, line 18 – column 3, line 5 column 3, line 25 – line 55 -----	1-18
A	US 3 945 843 A (HOLTY DAVID W ET AL) 23 March 1976 (1976-03-23) column 1, line 5 – line 62; claims 1,6-8 -----	1-18
A	EP 1 160 201 A (HUBER CORP J M) 5 December 2001 (2001-12-05) paragraph '0001! – paragraph '0002! paragraph '0034! -----	
A	EP 0 491 391 A (ALBRIGHT & WILSON) 24 June 1992 (1992-06-24) cited in the application page 3, line 4 – line 22 -----	1,7,8

INTERNATIONAL SEARCH REPORT

International Application No

/GB2004/000056

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 0208127	A 31-01-2002	AU 7080101 A CA 2416465 A1 CN 1458907 T DK 200300053 A WO 0208127 A1 GB 2379440 A ,B NO 20030230 A US 2003226808 A1		05-02-2002 31-01-2002 26-11-2003 13-03-2003 31-01-2002 12-03-2003 12-03-2003 11-12-2003
US 6180056	B1 30-01-2001	AU 755347 B2 AU 2047500 A CN 1329578 T EP 1149055 A1 ID 30044 A TW 510893 B WO 0034190 A1		12-12-2002 26-06-2000 02-01-2002 31-10-2001 01-11-2001 21-11-2002 15-06-2000
WO 9933345	A 08-07-1999	AT 226393 T AU 736266 B2 AU 2275399 A CA 2316363 A1 DE 69808968 D1 DE 69808968 T2 DK 1041885 T3 WO 9933345 A1 EP 1041885 A1 ES 2186252 T3 JP 2001527028 T NO 20003267 A NZ 505301 A PT 1041885 T TW 492840 B		15-11-2002 26-07-2001 19-07-1999 08-07-1999 28-11-2002 11-09-2003 17-02-2003 08-07-1999 11-10-2000 01-05-2003 25-12-2001 02-08-2000 31-05-2002 31-03-2003 01-07-2002
WO 0004777	A 03-02-2000	AU 5005399 A BR 9912341 A CA 2337953 A1 CN 1313728 T EP 1098566 A1 ID 27376 A JP 2002521313 T NO 20010317 A WO 0004777 A1		14-02-2000 02-10-2001 03-02-2000 19-09-2001 16-05-2001 05-04-2001 16-07-2002 22-03-2001 03-02-2000
US 4673509	A 16-06-1987	AT 32330 T AU 563765 B2 AU 3247384 A CA 1245126 A1 DE 3469162 D1 EP 0139404 A1 FI 843357 A ,B, GB 2145708 A ,B JP 1841615 C JP 5050481 B JP 60072807 A KR 9109128 B1 NO 843399 A ,B, ZA 8406638 A		15-02-1988 23-07-1987 28-02-1985 22-11-1988 10-03-1988 02-05-1985 27-02-1985 03-04-1985 12-05-1994 29-07-1993 24-04-1985 31-10-1991 27-02-1985 27-11-1985

INTERNATIONAL SEARCH REPORT

National Application No

P/GB2004/000056

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0839956	A 06-05-1998	EP 0839956 A2		06-05-1998
		US 6315867 B1		13-11-2001
		US 2002144797 A1		10-10-2002
US 3597251	A 03-08-1971	NONE		
US 3945843	A 23-03-1976	CA 1038523 A1		12-09-1978
		JP 51012391 A		30-01-1976
		JP 58031211 B		05-07-1983
EP 1160201	A 05-12-2001	US 6402824 B1		11-06-2002
		CA 2347547 A1		26-11-2001
		EP 1160201 A2		05-12-2001
EP 0491391	A 24-06-1992	AT 137756 T		15-05-1996
		AU 2009295 A		18-04-1996
		AU 667295 B2		21-03-1996
		AU 8978491 A		25-06-1992
		BR 9105481 A		01-09-1992
		CA 2057822 A1		19-06-1992
		DE 69119377 D1		13-06-1996
		DE 69119377 T2		26-09-1996
		DK 491391 T3		28-05-1996
		EP 0491391 A1		24-06-1992
		ES 2090222 T3		16-10-1996
		FI 915967 A		19-06-1992
		GB 2252322 A , B		05-08-1992
		GR 3020264 T3		30-09-1996
		JP 3225213 B2		05-11-2001
		JP 10072476 A		17-03-1998
		JP 2833895 B2		09-12-1998
		JP 4334392 A		20-11-1992
		KR 249658 B1		01-04-2000
		MX 9102651 A1		01-11-1992
		NO 915002 A		19-06-1992
		SG 54156 A1		16-11-1998
		US 5606105 A		25-02-1997
		US 5386038 A		31-01-1995
		ZA 9109861 A		25-11-1992